

## **MECHANICAL AND CORROSION RESISTANCE PROPERTIES OF NANO TiO<sub>2</sub> REINFORCED NI COATINGS**

**VINUTH H S, PRASHANT M CHOUDRI, HUSAINBASHA J BALLARI, PRAJWAL PANJI,  
AKASH ARMANI**

B.V. Bhoomaraddi College of Engineering & Technology, Vidyanagar, Hubli, Karnataka, India

### **ABSTRACT**

TiO<sub>2</sub> is in great choice for the generation of composite coatings on steel, due to its increasing availability and to the fact that TiO<sub>2</sub> can reinforce into electroplate to improve the mechanical properties and other properties such as magnetic and photocatalytic properties etc [5].

In this context, the aim of this work is to investigate the influence of the nature and concentration of nano particles on the corrosion resistance of the composite films plated on steel substrate by the electrochemical by polarization curves and non-electrochemical methods wear resistance, SEM, XRD studies were conducted to analyze the properties.

**KEYWORDS:** Mechanical and Corrosion Resistance Properties of Nano TiO<sub>2</sub> Reinforced Ni Coatings, SEM, XRD Studies

### **INTRODUCTION**

Corrosion problems are found in all aspects of technology. It is a matter of great economic and technical concern. The annual losses due to corrosion are approximately 3-4% of GNP in many advanced and developing countries. Steel is the widely used material in industries owing to its low cost and potential properties. Although, galvanizing protects the corrosion of steels its application is limited. Several coating techniques have been developed to protect materials[1]; among them the composite coating containing nanoparticles is proved to be the best technique to develop a corrosion resistant material along with the additional properties[2].

Now a days there is a lot of scope on the development of nano composite coating on steel substrates because of its low cost and versatility. These composite materials can be used even at high temperature and pH. These improved characteristics may be due to the combined inherent properties of nanoparticles and the deposited metal [3].

Composite coating is a method of co-depositing fine particles with a metal or alloy matrix. During this process, these insoluble particles are suspended in a conventional plating electrolyte and are captured in the growing metal film. As a result the produced coatings will have superior corrosion resistance and mechanical properties. From the past literature survey, certain nano size materials like ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> have been incorporated in the nickel matrix by the electrodeposition technique and obtained an average coating thickness of about 10-13 μm, to form nano composite coating on steel for the improvement corrosion resistance and wear resistance [4]. Several studies have been found that the co-deposition of nano-sized or sub micron particles with metal matrices are superior to micron-sized particles on qualities of composite coatings [5]. The presence of nanoparticles in the deposit induces its inherent properties like high hardness, chemical and mechanical stability to the coating. So it makes the deposit to more corrosion resistant [6].

With these considerations, in order to improve wear resistance, many investigators have successfully attempted to co-deposit hard particles (like  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{SiC}$ ,  $\text{WC}$ ,  $\text{Cr}_3\text{C}_2$ ,  $\text{TiC}$ , diamond, etc.) in a range of metal matrices such as Ni, Cr, Co, Re, etc. Fine oxide particles of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  were also co deposited on steel as a base metal and achieved the desired properties [7].

Among the nanomaterials,  $\text{TiO}_2$  is in great choice for the generation of composite coatings on steel, due to its increasing availability and to the fact that  $\text{TiO}_2$  can reinforce into electroplate to improve the mechanical properties and other properties such as magnetic and photocatalytic properties etc [8].

Several authors have studied the  $\text{TiO}_2$  as reinforcing material in Ni, Zn and its alloys on copper or steel for the improvement of mechanical properties [9]. Even though large no of researchers are working on mechanical properties and photocatalytic activities of Ni –  $\text{TiO}_2$  composites.

In this context, the aim of this work is to investigate the influence of the nature and concentration of nano particles on the corrosion resistance of the composite films plated on steel substrate by the electrochemical (polarization curves, electrochemical impedance spectroscopy) and non electrochemical methods(wear resistance, SEM, XRD) were tested.

## EXPERIMENTAL

Analytical grade chemicals and millipore water were used for the preparation of Ni bath solution. The Ni- $\text{TiO}_2$  composite coatings was electrodeposited on mild steel of specimens of dimension  $5 \times 4 \times 0.1$  cm from the Ni bath solution containing 100 mg/L of  $\text{TiO}_2$ . The pure Ni deposits were obtained from Ni bath solution without  $\text{TiO}_2$ . composition is given in table 1. The bath solution containing the  $\text{TiO}_2$  was stirred using a magnetic stirrer at 600 rpm for about 24hr prior to the electrodeposition, and subsequently by ultrasonic agitation for 30 minutes just before electroplating, for the uniform distribution of particles in the bath solution. The equal surface area of Ni metal and mild steel specimens was used as the anode and cathode respectively for the electrodeposition process. The mild steel plates were mechanically polished with different grades of emery paper to get a smooth, bright and uniform surface area then before it is used for deposition process. The Ni metal plates were activated by dipping in 10% dil  $\text{HNO}_3$  solution. The electrodeposition process was carried out at a current density of  $1 \text{ A/dm}^2$  for 1h with 300 rpm solution stirring speed at  $40 \pm 5$  °C.[10]

Table 1

Bath Composition	$\text{gL}^{-1}$
NiSO <sub>4</sub>	32.26
Na <sub>2</sub> SO <sub>4</sub>	63.00
H <sub>3</sub> BO <sub>3</sub>	8.54
$\text{TiO}_2$	100 mg

## STRUCTURAL CHARACTERIZATION

The X-ray diffraction (XRD) patterns (PANalytical X'pert pro powder diffractometer,  $\lambda_{\text{CuK}\alpha} = 1.5418 \text{ \AA}$ , scanning rate of  $2^\circ/\text{minute}$  in the  $2\theta$  range  $10^\circ$ - $90^\circ$  working at 30 mA and 40 kV) were used for the phase analysis and crystalline size determination. Morphological analysis was also confirmed by scanning electron microscope (SEM, Philips XL 30) fitted with an energy dispersive X-ray diffraction analyzer (EDAX)[12]. The hardness of the coatings was measured by "Clemex microhardnes Tester" made in Japan using Vickers diamond as indenter at a load of 50 and 100 g for a loading time of 5 s. The average value of five indentations was recorded for an exposed area of  $1 \text{ cm}^2$ . [11]

## ELECTROCHEMICAL CORROSION CHARACTERIZATION

The electrochemical corrosion studies were performed in a conventional glass cell by using CHI 660C electrochemical work station (US made) at  $27 \pm 2$  °C. The Ni and Ni- TiO<sub>2</sub> coated steel specimen, platinum wire and a saturated calomel electrode (SCE) were used as working, auxiliary and reference electrodes. The working electrodes of 1cm<sup>2</sup> were employed for corrosion studies in 3.5% NaCl solution.[12]

## WEAR TEST USING BALL ON DISK TRIBOTESTER

The wear tests were evaluated on a reciprocating ball-on-disk computer-controlled oscillating tribotester. A tungsten carbide (WC) ball with diameter 6 mm used as a counter body. All the wear tests were performed using a load of 1.5kg at  $12 \times 10^{-3}$  m/s sliding speed in dry condition at room temperature. The total sliding distance is 10m.

## RESULTS AND DISCUSSIONS

X-ray diffractograms of the Ni and Ni-TiO<sub>2</sub> coatings were shown in the Figure 1 where Figure 1a represents the diffractogram of the Ni coating and Fig 1b represents that of Ni- TiO<sub>2</sub> composite coating. The average crystallite size of the deposits was calculated from the Debye Sherrer equation 1

$$L = \left( \frac{K \lambda}{\beta \cos \theta} \right) \quad [16] \quad (1)$$

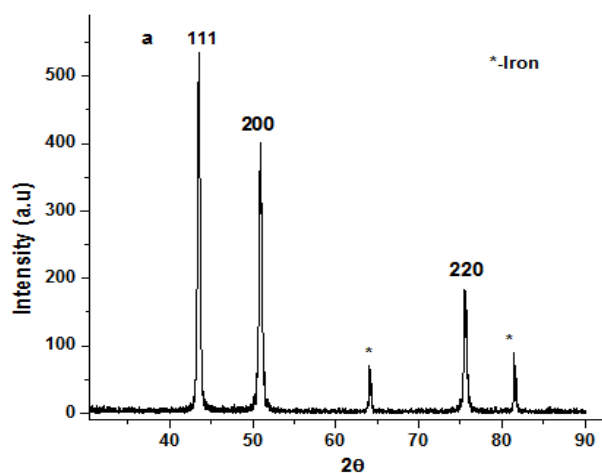


Figure 1(a)

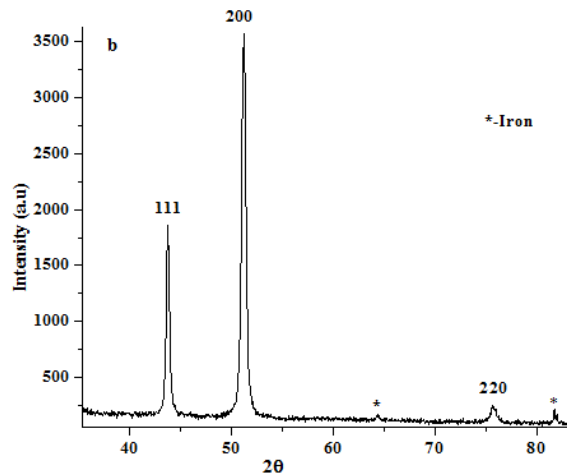


Figure 1(b)

Where  $L$  = average crystallite size,  $K$  - Scherrer constant,  $\lambda$  - wave length,  $\beta$  - Full width half maxima,  $\theta$  - diffraction angle. The average crystallite size of composite coating was 20.12 nm against the 30 nm of Ni coating. This reduction in the crystallite size of the composite coating was further supported by the increase in peak width of the diffractograms of the composite deposit. Also it is observed from the figure that there is an increase in the intensity of 111 and 200 peaks. This increase in peak width and the intensity will suggest the influence of  $\text{TiO}_2$  during the Ni electrodeposition process. Iron peaks which are prominently observed in the Ni electrodeposits have very less intense peaks in the Ni composite coating it suggests that the presence of  $\text{TiO}_2$  in the composite coating influence the more Ni deposition by filling micron sized holes or cracks which usually forms during the electrodeposition of Ni.

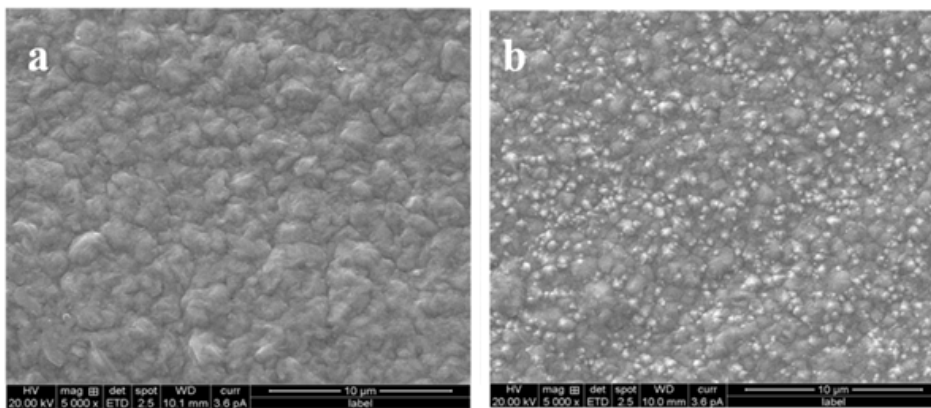


Figure 2

Figure 2 The SEM micrographs of the electroplated Ni coatings in the presence and absence of  $\text{TiO}_2$ . Fig a represents the surface morphology pure Ni coating and Figure b shows that of Ni- $\text{TiO}_2$  composite coating. It is observed from the figure that composite coated shows a more uniform, bright and smaller grain sized image compared to the bare Ni coating. Furthermore the images revealed that the  $\text{TiO}_2$  adsorbed on to the plating surface during deposition and influence nucleation growth of composite, resulting in fine grained and intact arrangement of Ni crystals in the deposit.

Vickers microhardness measurements were performed to the electrodeposited Ni and Ni-TiO<sub>2</sub> coatings and were shown in the Figure 3. Microhardness of the Ni-TiO<sub>2</sub> coatings was higher than that of that of the electrodeposited Ni. The microhardness of the composite coatings increased due to the uniform distribution of TiO<sub>2</sub> in the metal matrix and fine grained structure of the composite.

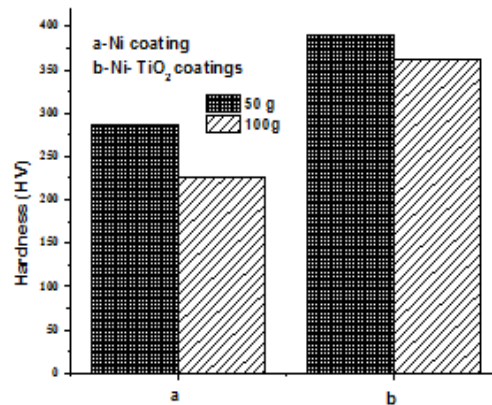


Figure 3

The presence of TiO<sub>2</sub> in the fine grained metal matrix obstruct the easy movement of dislocations and resist plastic flow also the inherent high mechanical strength of TiO<sub>2</sub> made them to acquire higher micro hardness property to the composites. To test the protective ability of the Ni and Ni-TiO<sub>2</sub> coatings were carried out polarization measurements.

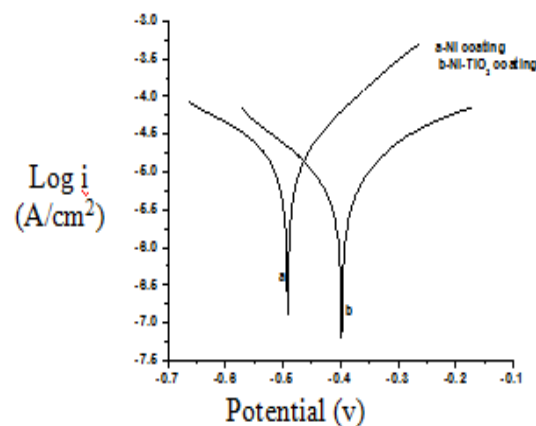


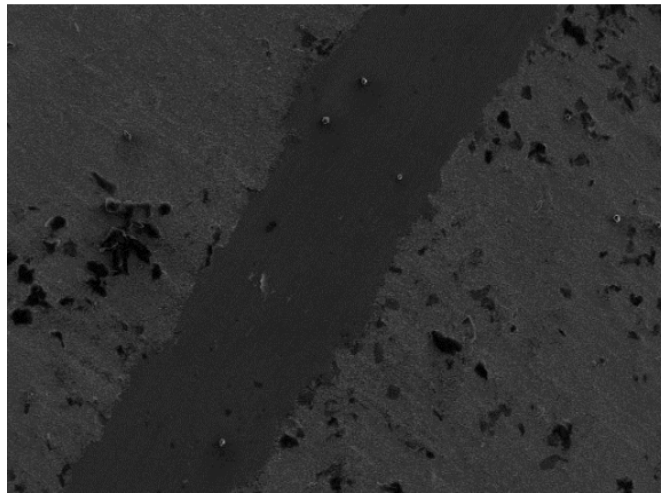
Figure 4

Table 2

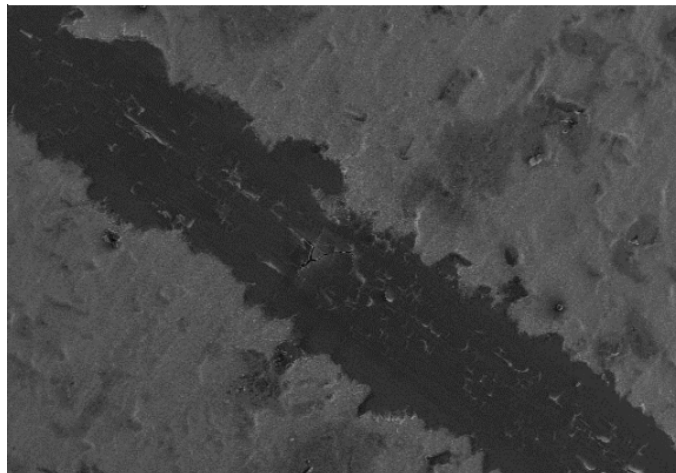
Sample	I <sub>corr</sub> (A cm <sup>-2</sup> )	E <sub>corr</sub> (V)	Corrosion Rate (mil y <sup>-1</sup> )
Ni	1.58×10 <sup>-5</sup>	- 0.492	2.96
Ni- TiO <sub>2</sub> composite coating	6.687×10 <sup>-6</sup>	- 0.398	0.90

The corrosion resistance behavior of the Ni and Ni TiO<sub>2</sub> coatings of 1 cm<sup>2</sup> area was evaluated by Tafel polarization studies[16]. The coated specimens of 1 cm<sup>2</sup> area were immersed in 3.5% NaCl solution for the duration of 5 minutes to attain an equilibrium potential. The electrodes were then polarized cathodic to anodic direction in the potential

range of  $\pm 200\text{mV}$  from the OCP at a scan rate of  $0.01\text{V/s}$ . The corrosion current densities were determined by extrapolating linear portion of the anodic and cathodic curves. Fig 4 shows the Tafel curves of the deposits Ni (curve “a”) and Ni-TiO<sub>2</sub>(curve “b”) coatings. From the figure 4 it is observed that Ni- TiO<sub>2</sub>composite coatings curve is shifted to more positive potential compared to the bare Ni deposit indicating the more noble character of Ni- TiO<sub>2</sub>coatings and also its  $i_{\text{corr}}$  value is significantly decreased relative to the Ni deposit. This shift of corrosion potential and decrease in  $i_{\text{corr}}$  value indicates the anti corrosive properties of the composites. This high corrosion resistance property of the composites is may be due to the fact that the presence of TiO<sub>2</sub>in the Ni deposit increases the nucleation rate and retards the crystal growth which leads to the reduction in the grain size of the composite coatings. Hence becomes responsible for the high corrosion resistance property of the composite coatings.



**Figure 5a**



**Figure 5b**

Figure 5a and 5b shows SEM of the worn out surfaces of the Ni and NiTiO<sub>2</sub> coating respectively at the resolution of  $500\mu\text{m}$ . According to the experimental results the wear rate of the specimen with nano coating of NiTiO<sub>2</sub> was found to be lesser than the specimen with Ni coating. Wear resistance of the nanocomposite coating was 38% greater than than the wear resistance of the Ni coating. The increase in the wear resistance is due to the accumulation of the finer particles on the coating which results in reduction of friction at the contact surface. This results in higher wear resistance of TiO<sub>2</sub> reinforced nano coatings.

## CONCLUSIONS

From XRD test the average crystallite size of composite coating was 20.12 nm against the 30 nm of Ni coating. From SEM analysis it is found that composite coated shows a more uniform, bright and smaller grain sized image compared to the bare Ni coating. From the tuffel curves, composite coated specimen shown about 25% greater corrosion resistance than the Ni coated specimen. through the wear test, composite coated specimen shown about 33% greater wear resistance than the normal Ni coated specimen.

Hence, reinforced Ni nanocomposite coatings revealed a much smoother surface microstructure with excellent mechanical properties.

## REFERENCES

1. Baolei Han, Xinchun Lu *Surface & Coatings Technology*, 203 (2009) 3656-3660.
2. W. Metzger, R.oft, G. Laux, H. Harst *galvotechnik*, 61 1 (1970) 998.
3. M. A. Willard, *Int .Mat.Rev.*, 49, (2004), 125.
4. N. Ichinose, Y. Ozaki and S. Kashu, *Superfine particle technology* Springer-Verlang, London, (1992).
5. X. G. Li, A. Chiba and S. Takahashi, *J. Magn.Magn.Mater.*, 170 (1997), 339.
6. A. Tucciarone, *J. Magn.Magn.Mater.*, 20 (1980), 111
7. Shan Guan, Bradely J. Nelson and Karl Vollmers, *Journal of electrochemical Society*, 1519 (2004), 545.
8. C. T. J. Low, R. G. A. Wills, *Surface & Coatings Technology*, 201, (2006) 371.
9. G. Wu, N. Li, D. Zhou, K. Mit Suo, *Surface & Coatings Technology*, 176, (2004) 157.
10. C. Muller, M. Sarret, M. Benbella, *Surface & Coatings Technology*, 162 (2003) 162.
11. S. Iwasaki and Nakamura, *IEEE Trans. Magn.*, MAG-13 (1997), 1272.
12. M. Surender, R. Balasubramaniam and B. Basu, *Surface & Coatings Technology*, 187 (2004) 93– 97.

